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Calcination of Calcium-Based Sorbents for Control of SO_2 Emissions from Coal Fired Boilers

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16. ABSTRACT The paper summarizes the results of an experimental study that focused on the production of high surface area materials from various sorbents. (NOTE: Injecting calcium-based sorbents into coal burning utility boilers to control SO2 emissions is being considered by the EPA as an acid rain control technology because capital equipment requirements are small and the process is entirely dry. Both theoretical calculations and experimental results indicate that SO2 capture is strongly related to the surface area of the calcined sorbent. Thus, an improved understanding of the formation of surface area is required for the complete optimization of the sorbent injection process.) Weight loss and B. E. T. surface area data were obtained as a function of residence time and furnace temperature for 14 different sorbents which were members of 4 distinct classes: limestones, dolomites, hydrated limes, and pressure hydrated dolomitic limes. The results demonstrate major differences between classes of sorbents. In general, the hydrated limes calcined faster and produced higher surface areas than the corresponding carbonates. The dolomitic materials also produced higher surface areas than the comparable calcitic sorbents. Pressure hydrated dolomitic limes performed the best, producing surface areas in excess of 140 sq m/g; the limestones performed the worst.

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Area	Combustion	Stationary Sources	12A	21B
Calcines	Limestone	Surface Area	11B	08G
Sorbents	Dolomite	Hydrated Lime	11G	
Sulfur Dioxide	Calcium Oxides	Dolomitic Lime	07B	
Emission			14G	

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ABSTRACT

The injection of calcium-based sorbents into coal burning utility boilers to control SO_2 emissions is currently being considered by EPA as an acid rain control technology because capital equipment requirements are small and the process is entirely dry. Both theoretical calculations and experimental results indicate that SO_2 capture is strongly related to the surface area of the calcined sorbent. Thus, an improved understanding of the formation of surface area is required for the complete optimization of the sorbent injection process.

This paper summarizes the results of an experimental study which focused on the production of high surface area materials from various sorbents. The calcination process was decoupled from sulfation by batch calcining 3 g samples of calcium based sorbents (to produce CaO) for varying times in an electric furnace without SO_2 present. Nitrogen was blown through the furnace to prevent buildup of product species. Samples were stored in a nitrogen atmosphere to inhibit recarbonation and rehydration. Weight loss and B.E.T. surface area data were obtained as a function of residence time and furnace temperature for 14 different sorbents which were members of 4 distinct classes: 1) limestones, $CaCO_3$; 2) dolomites, $CaCO_3 \cdot MgCO_3$; 3) hydrated limes, $Ca(OH)_2$; and 4) pressure hydrated dolomitic limes, $Ca(OH)_2 \cdot Mg(OH)_2$. The 14 sorbents were compared after calcination at 700° C for 20 minutes. In addition, three sorbents were tested over a more extensive range of conditions.

As expected, the results demonstrate major differences between classes of sorbents. In general the hydrated limes calcined faster and produced

higher surface areas than the corresponding carbonates. The dolomitic materials also produced higher surface areas than the comparable calcitic sorbents. Pressure hydrated dolomitic limes performed the best, producing surface areas in excess of 140 m^2/g; the limestones performed the worst, calcining most slowly and producing the lowest surface areas.

The surface area data indicate the existence of three simultaneous, competitive processes: calcination with growth in surface area, catalyzed sintering which causes a rapid decrease in surface area, and deadburn sintering which results in a slow surface area loss. Deadburn sintering appears to only be significant above 700° C. Each of the competitive processes dominates in a particular regime during the overall calcination process.

In general, the surface areas obtained in this isothermal, inert calcination study correlate with SO_2 capture data taken in a small scale furnace at 1090° C, suggesting that, although the characteristic time constants are much shorter in an actual furnace environment, the controlling mechanisms are the same.

INTRODUCTION

Sulfur dioxide emissions from coal burning utility boilers have been implicated as major contributors to the acid rain problem. One potential technology for controlling SO_2 emissions is the injection of calcium-based sorbents into these boilers. The major advantages to this technology are that capital equipment requirements are small and the process is entirely dry.

Extensive research has been done on the capture of SO_2 by calcined sorbents. Both theoretical calculations and experimental results indicate that the SO_2 capture is strongly related to the surface area of the calcined sorbent, Borgwardt, et al., (1984). However, the formation and loss of surface area during and after calcination (sorbent activation) is not well understood. Thus, an improved understanding of surface area formation is required for the complete optimization of the sorbent injection process. Borgwardt, et al., (1984) studied the sintering (decrease in surface area) of CaO produced from limestone under differential conditions and found that the rate of sintering increased with both temperature and CO_2 partial pressure. Because the tests were all conducted outside the region where recarbonation could occur, he concluded that CO_2 catalyzes the CaO sintering process. Borgwardt (1985) also studied the development of surface area by limestone particles calcined in an entrained flow reactor and concluded that CaO has a maximum in surface area immediately following $CaCO_3$ decomposition. Borgwardt noted also that the sintering rate is independent of particle size.

This paper summarizes the results of an experimental study which

focused on the production of high surface area sorbents. The sorbents chosen for this study were selected because of commercial availability and use in other EPA research programs. In order to study the surface area formation of the sorbents, the calcination process was decoupled from the sulfation process by calcining in a carefully controlled, SO_2-free environment.

The sorbents used in this study as members of the four distinct classes of calcium-based materials currently being considered for SO_2 control:

1) limestones, $CaCO_3$

2) dolomites, $CaCO_3 \cdot MgCO_3$

3) atmospheric hydrated calcitic limes, $Ca(OH)_2$

4) pressure hydrated dolomitic limes, $Ca(OH)_2 \cdot Mg(OH)_2$

The calcination reactions are:

$$CaCO_3 = CaO + CO_2$$

$$Ca(OH)_2 = CaO + H_2O$$

and the sulfation reaction is:

$$CaO + SO_2 + \tfrac{1}{2}O_2 = CaSO_4$$

EXPERIMENTAL METHODS

Samples (3 g) of calcium based sorbents were batch calcined in 6 in. (15 cm) quartz boats for varying lengths of time in an electric furnace. See Figure 1. Preliminary tests had shown that sample size in the range 1 to 5 g did not affect surface area. Nitrogen gas was blown through the furnace for the duration of the experiment to prevent any buildup of product species. A sweep ratio (volume of inert/volume of product) of at least 300 was required to maximize the product surface area. Calcined samples were

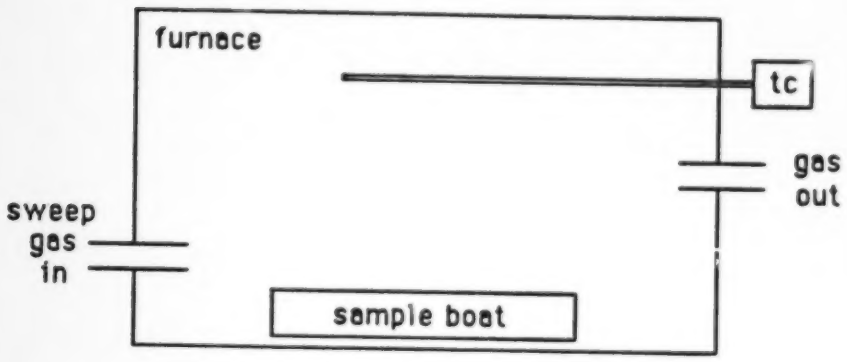

Figure 1. Batch Calcination in Inert Atmosphere

stored in a nitrogen atmosphere prior to B.E.T. analysis to inhibit recarbonation and rehydration. Additional preliminary tests showed that the surface areas of samples stored in vials open to the atmosphere dropped exponentially with time (presumably due to rehydration) while those stored in closed containers did not.

Weight loss and B.E.T. surface area data were obtained as a function of residence time and furnace temperature. Percent conversion was calculated from weight loss data.

Table 1 lists the commercial sorbents used for the initial detailed investigations. These materials were selected because they had been used in other, larger-scale EPA test programs. Initial surface area and mean size data are also presented.

Table 1. Sorbent Class Representatives

	Class	Major Components	Representative	Initial Surface Area (m^2/g)	Mean Size (μm)
LS	limestone	$CaCO_3$	Vicron 45-3	0.9	11
AHC	atmospheric hydrated lime	$Ca(OH)_2$	Longview	15.9	4
PHD	pressure hydrated dolomitic lime	$Ca(OH)_2$ $Mg(OH)_2$	Genstar S	25.3	1.4

DISCUSSION

TYPICAL TIME-RESOLVED RESULTS

The first set of experiments following the preliminary screening tests

was designed to evaluate the influence of thermal history on the development and loss of surface area. These studies utilized Genstar S representing the pressure hydrated dolomitic class. Temperatures for these experiments varied from 200 to 980° C, and residence times ranged from 30 seconds to 80 minutes. Figure 2a shows surface area as a function of time for the lower temperatures. The 25 m^2/g surface area of the uncalcined Genstar S is included on the plot at time zero. Large, initial rates of surface area growth are seen above 315° C. Maximums in surface area occur at 155 m^2/g for 60 minutes and 370° C and at 100 m^2/g for 5 minutes and 540° C. No change in surface area is observed beyond 15 minutes at 540° C.

Figure 2b shows surface area versus time for the higher temperatures. Again, the surface area of uncalcined Genstar S is included. The growth of surface area occurs so fast that it is not experimentally observed. A high rate of decrease in surface area is initially observed for all temperatures. This rate increases with temperature. No change in surface area is seen after 7 minutes at 700° C and after 2 minutes at 870° C. Surface area decreases slowly after 2 minutes at 980° C.

Figure 3 shows conversion versus time for the entire temperature range. At 370° C and below, an asymptotic approach to the final conversion level is observed, while above 370° C the final conversion is achieved quickly. A final conversion value is not seen for 315° C. Conversion data for both 870 and 980° C fall practically on the same line. Table 2 gives the time required to reach final conversion at each temperature.

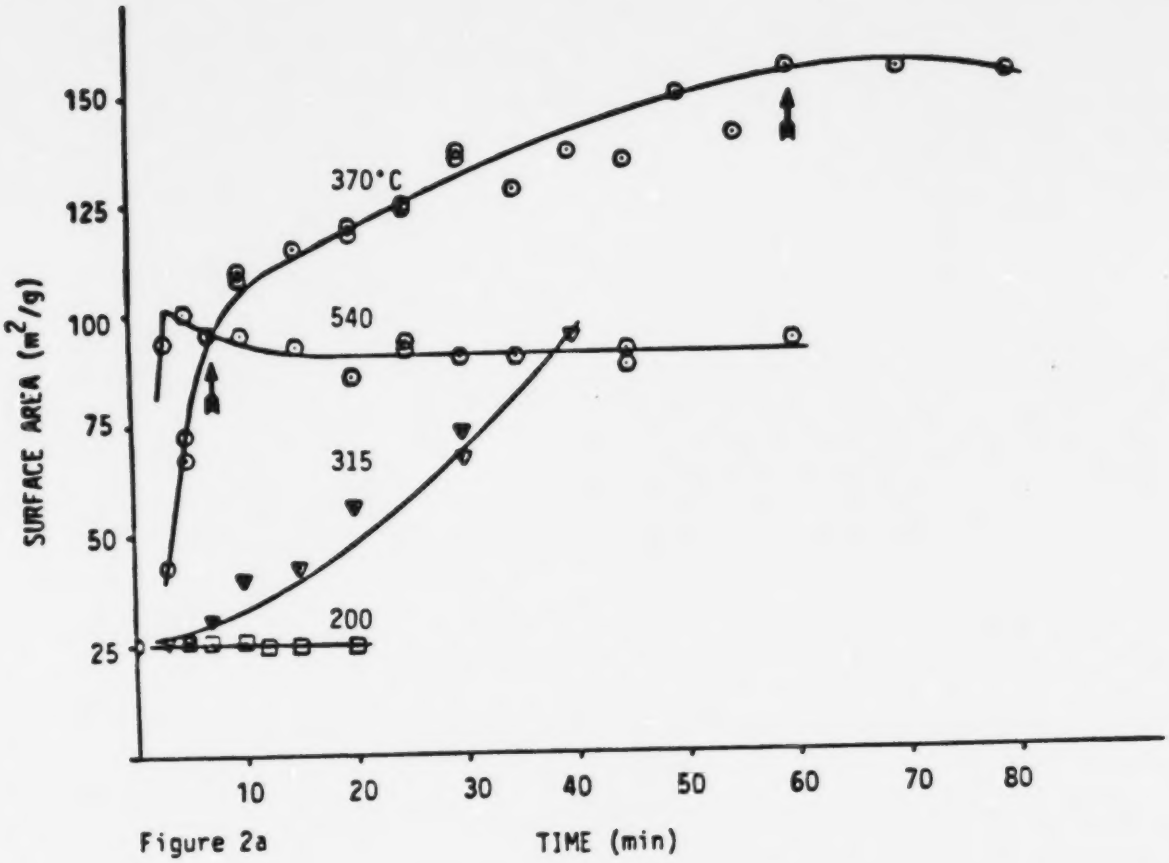

Figure 2a

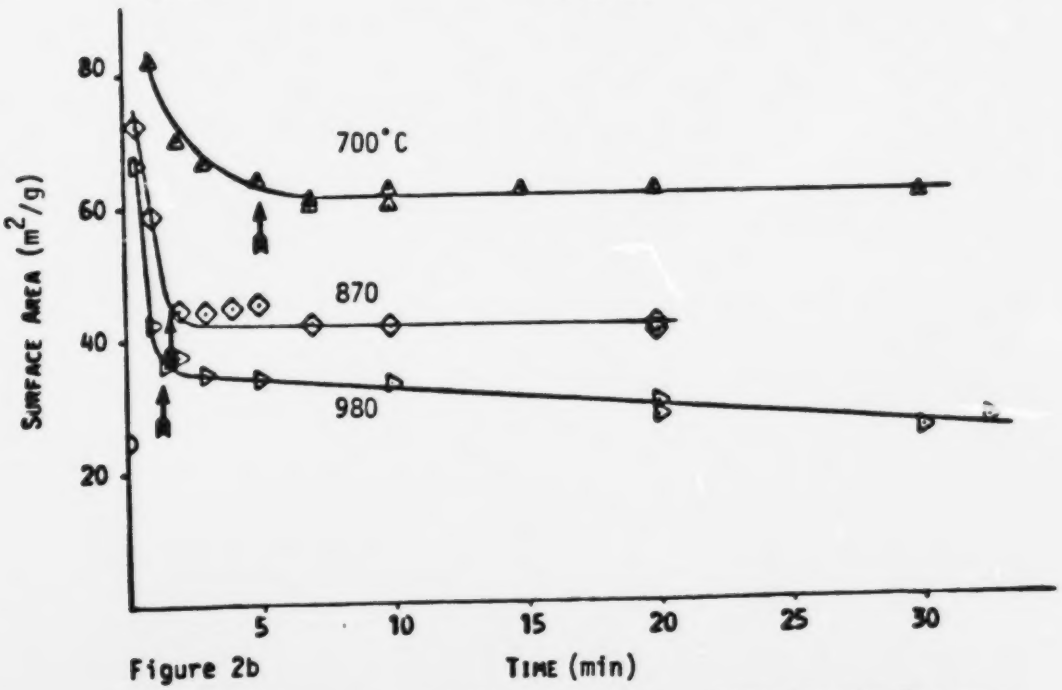

Figure 2b

Figure 2a,b. Surface Area Versus Time for the Pressure Hydrated Dolomitic Lime, Genstar S (3.0 g, N_2 sweep @ 1.47 m^3/h (0° C)). (Arrows indicate points of complete calcination.)

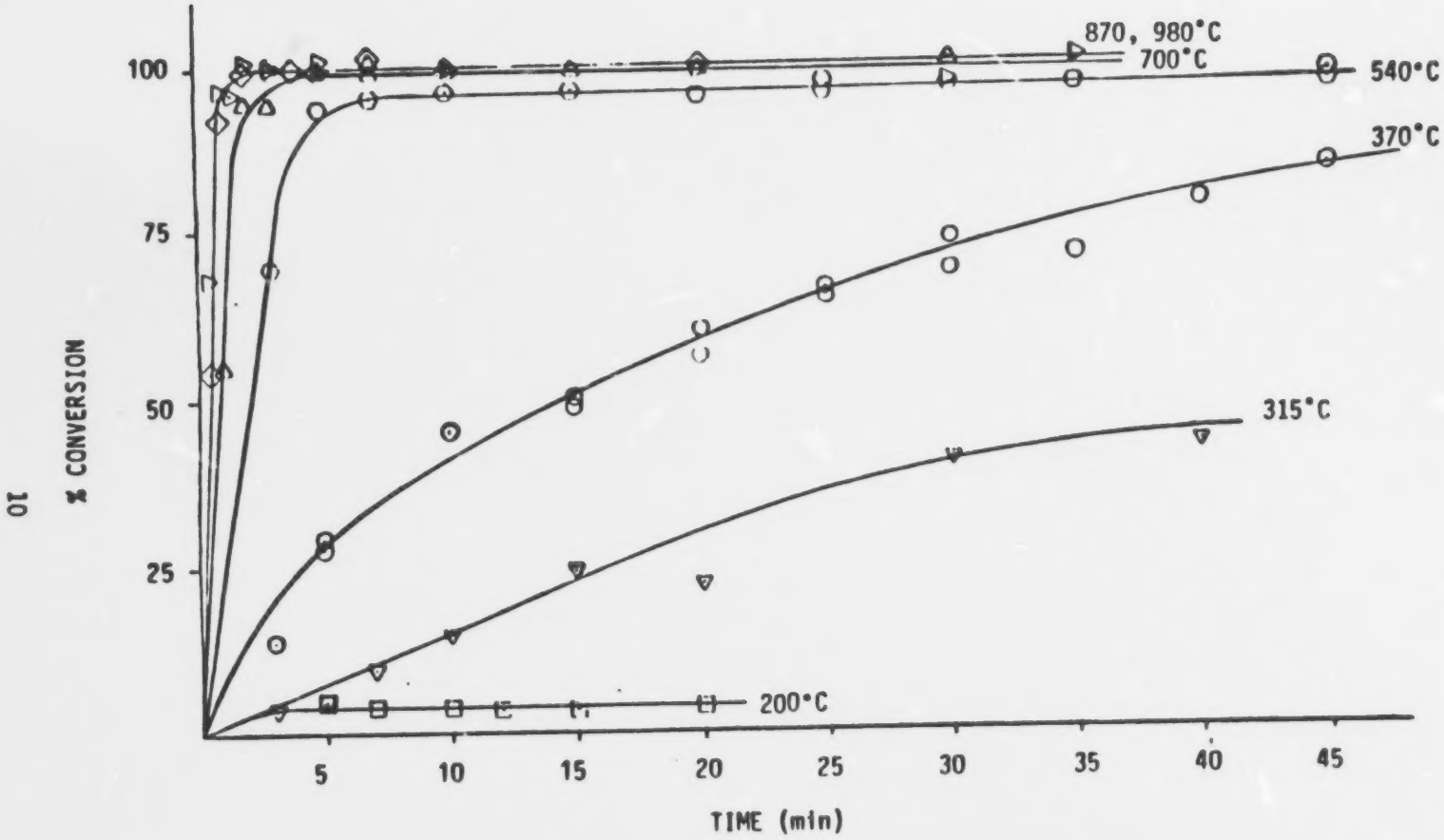

Figure 3. Extent of Reaction Versus Time for the Pressure Hydrated Dolomitic Lime, Genstar S (3.0 g, N_2 sweep @ 1.47 m^3/h (0° C)).

Table 2. Time Required for Complete Calcination of Genstar S

Temperature	Time
370° C	60 min
540	8
700	5
870	2
980	2

The observed behavior of surface area with time can be explained by three simultaneous, competing steps each of which dominates in a particular regime. The three competing steps can be simply represented as:

$$Ca(OH)_2 \xrightarrow[\Delta]{} CaO^* + H_2O \qquad (1)$$

$$CaO^* \longrightarrow CaO \quad \text{(fast)} \qquad (2)$$

$$CaO^* \xrightarrow[\Delta]{H_2O} CaO \quad \text{(slow)} \qquad (3)$$

where CaO* represents a highly reactive, high surface area lime with an open, microporous grain structure.

Step (1) is the thermal decomposition of calcium hydroxide to produce a high surface area (active) calcium oxide and water vapor. Step (2) is the sintering of the high surface area calcium oxide in the presence of water vapor to produce a low surface area calcium oxide (catalyzed sintering). The data shown in Figure 2b suggest that Step (2) is fast. Physically this sintering probably corresponds to grain growth and coalescing of the micropores. Step (3) is the thermal sintering (deadburning) of the high surface area calcium oxide, a step that occurs slowly. The rate of each of the three reactions is temperature dependent.

During calcination, each of these three reactions may occur, and even dominate, at different radial locations within a particular particle. At

very high temperatures (>1200° C) it appears likely that sintering may simply follow the calcination front through the particle and high (overall) surface areas never exist. However, at the condition of this study the three competing reactions lead to three distinct regimes, and in each regime one of the competing steps dominates. When the reaction begins with unreacted calcium hydroxide there are neither product gases nor high surface area CaO present. In this first regime reaction (1) dominates. Here, high surface area calcium oxide is produced rapidly.

As the reaction proceeds, the concentration of product gases and active CaO increases. Consequently, the rate of Step (2) increases, and ultimately the rate of Step (1) decreases because most of the reactant has been consumed. When the reaction (2) dominates, the second regime has begun and the surface area decreases rapidly.

The competition between the calcination reaction (1) and the catalyzed sintering reaction (2) determines the peak overall surface area which is measured experimentally. Figure 2 indicates that this apparent peak area decreases with increasing temperature which may suggest that the activation energy of the sintering exceeds that of the calcination.

When the reaction reaches completion the production of active CaO and water vapor ceases. The local water vapor concentration decreases due to molecular diffusion outward, and the rate of reaction (2) goes to zero. Hereafter, reaction (3) dominates, with the surface area slowly decreasing.

Comparison of Figures 2a,b with Figure 3 reveals that (1) surface area grows only during the reaction to form CaO, (2) catalyzed sintering begins before the reaction is complete and ends approximately when the calcination

reaches completion (indicated by the arrows in Figure 2), and (3) deadburn sintering, observed only at 980° C, is only apparent after the reaction has gone to completion and the N_2 sweep gas has removed the water vapor from the system.

COMPARISON OF SORBENT ALTERNATIVES

Figure 4 illustrates the surface area versus time results for each of the three sorbents. The 700° C data (Figure 4a) and the 980° C data (4b) both show that the rate of surface area growth is ordered pressure hydrated dolomitic>>hydrated calcitic>>limestone. Surface area growth of the hydrated calcitic sorbent is seen for the first 2 minutes at 700° C but is not seen at 980° C. For the limestone, growth is seen for 50 minutes at 700° C and for 5 minutes at 980° C. These times are less than or equal to those required to reach 100% conversion (see Table 3). Catalyzed sintering of the hydrated calcitic sorbent is over at about 3 minutes for both 700 and 980° C. Limestone does not experience catalyzed sintering at 700° C but at 980° C, catalyzed sintering of the limestone ends at 7 minutes. In all cases, catalyzed sintering ceases just after the reaction has gone to completion.

Table 3. Time Required for Complete Conversion of the LS and AHC Sorbents

	700° C	980° C
limestone (Vicron)	70 min	5 min
AHC (Longview)	4	2

Table 3 shows the time required for complete conversion of the

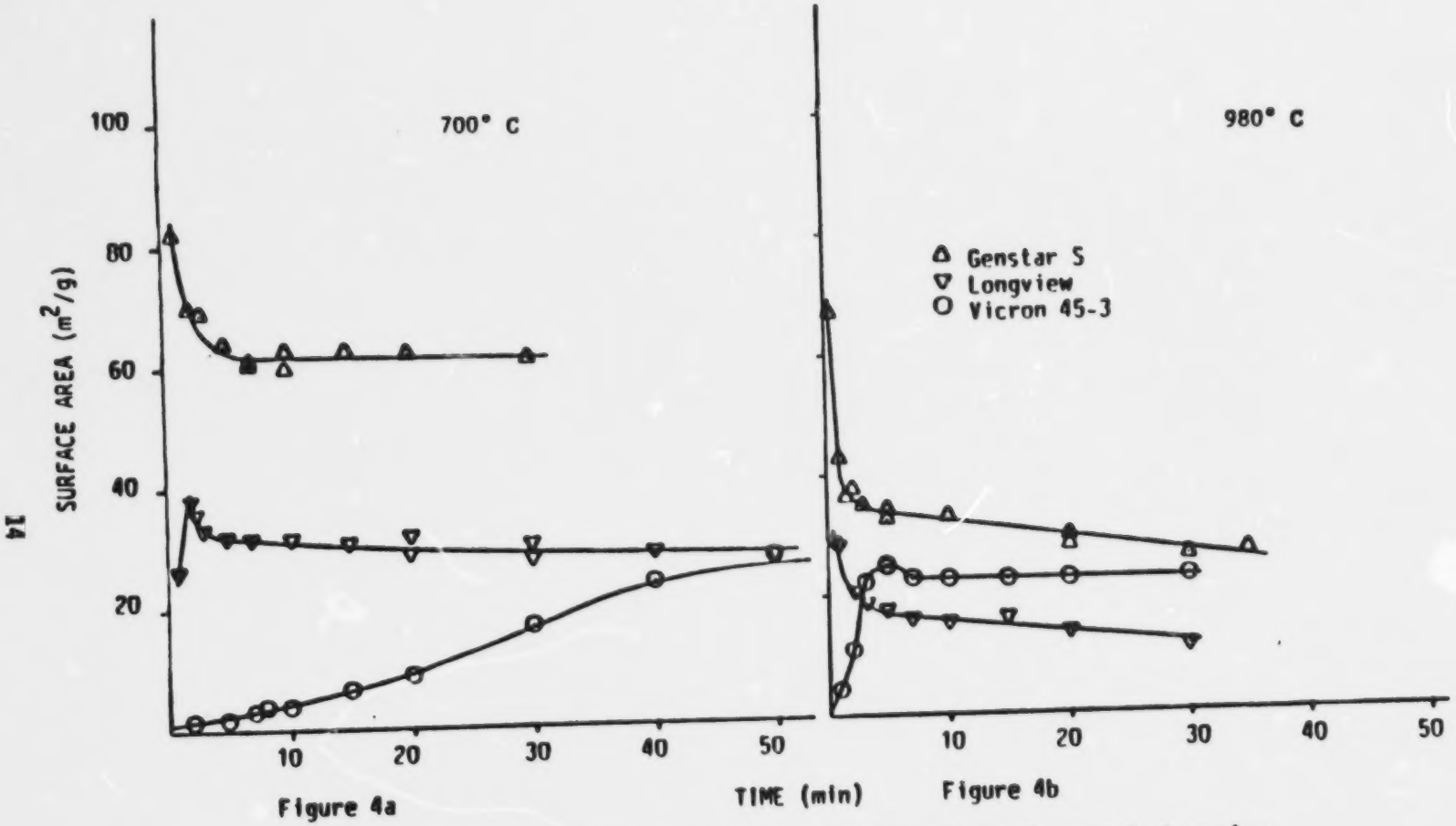

Figure 4a Figure 4b

Figure 4. Class Comparison of Surface Area Versus Time. Genstar S, Longview, and Vicron 45-3 (3.0 g, N_2 sweep @ 1.47 m^3/h (0° C)).

limestone and hydrated calcitic sorbents. These data demonstrate that dehydration occurs much faster than CO_2 evolution.

Slow deadburn sintering of the hydrated calcitic sorbent is observed at 700° C. At 980° C, the hydrated calcitic and the pressure hydrated dolomitic sorbents both experience deadburn sintering at about the same rate. Deadburn sintering is not seen for the limestone and is only seen for the hydrates at or above 700° C.

At 700° C, the surface areas are ranked pressure hydrated dolomitic>>hydrated calcitic>>limestone for short times and pressure hydrated dolomitic>>hydrated calcitic ≈ limestone for long times. At 980° C, surface areas are ranked pressure hydrated dolomitic>>hydrated calcitic>>limestone for short times and pressure hydrated dolomitic ≈ limestone>>hydrated calcitic for long times.

Figure 5 shows the same surface area data for the hydrated calcitic and limestone sorbents at 700° C; however, the ordinate is in terms of surface area per gram of calcium oxide. The curve for limestone now begins at its highest value and slowly decreases to a constant level after 20 minutes, even though the reaction does not go to completion until 70 minutes. The curve for the hydrated calcitic sorbent also begins at its highest value and rapidly decreases for approximately the first 4 minutes at which point dehydration is complete. Beyond this time only a slow decrease in specific surface area is observed.

These data suggest that the Longview atmospheric hydrate clearly exhibits the last two regimes, catalyzed sintering and slight deadburning. However, the Vicron limestone calcines so slowly (CO_2 evolution vs.

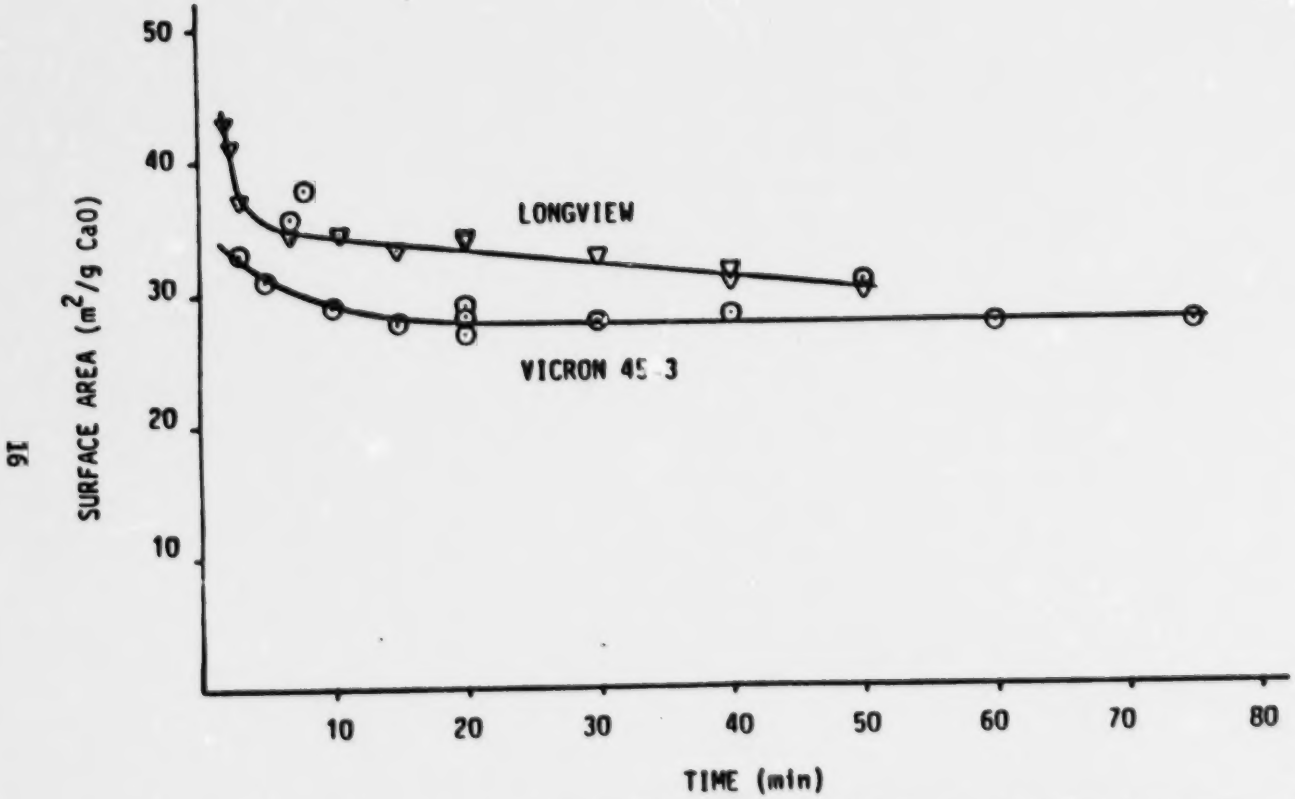

Figure 5. Surface Area per Gram of CaO Versus Time for Longview and Vicron 45-3 (700°C, 3.0 g, N_2 sweep @ 1.47 m^3/h (0° C)).

dehydration) that the catalyzed sintering follows the calcination front through the particle, and high specific surface areas are not observed (except very early in the calcination when the extent is very low).

EVALUATION OF COMMERCIAL SORBENTS

Figure 6 summarizes the surface areas of 14 sorbents grouped by class. All of the sorbents were calcined at 700° C for 20 minutes. These data indicate that:

(1) Hydrated sorbents produce higher surface areas than carbonated sorbents.

(2) Dolomitic sorbents are better than calcitic sorbents.

(3) Surface area differences between classes are generally much greater than variations within a specific class.

Because the hydrated sorbents calcine faster than the carbonated sorbents, they develop overall surface area at significantly higher rates. At the conditions of this comparison, 700° C and 20 minutes, this difference is pronounced; however, at very long times (>60 minutes) these differences vanish. Overall, the pressure hydrated dolomitic sorbents performed the best, reacting fastest, and producing the highest surface areas; the limestones performed the worst, calcining slowest, and producing the lowest surface areas. The difference in surface areas of the calcined pressure hydrated dolomitic and hydrated calcitic sorbents is larger than the difference in those of the uncalcined pressure hydrated dolomitic and hydrated calcitic sorbents. The same observation is made for the dolomites and limestones. Therefore, it appears that the presence of magnesium must lead to a smaller grain size and/or reduce the mean pore diameter, thereby

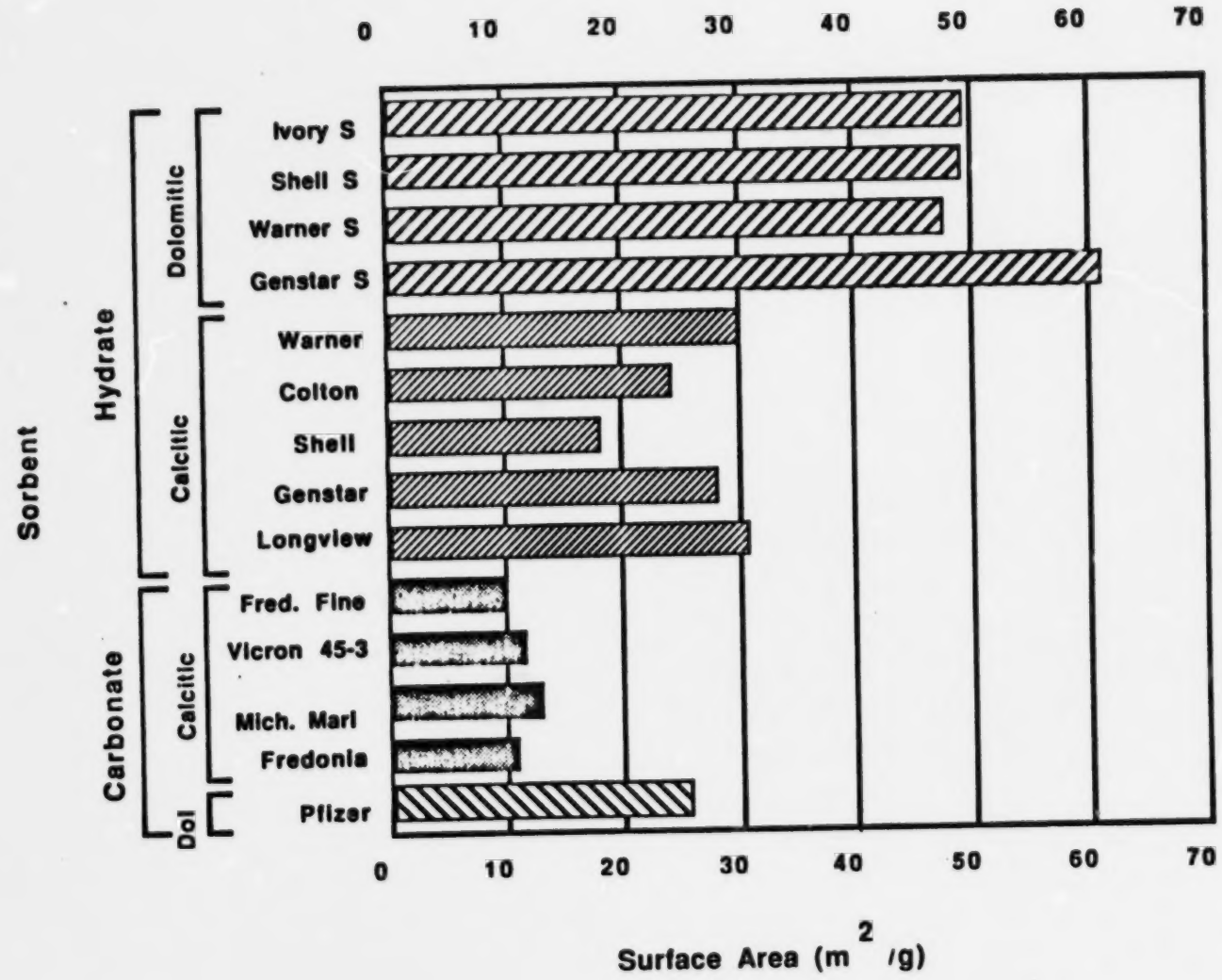

Figure 6. Comparison of Sorbent Surface Areas.

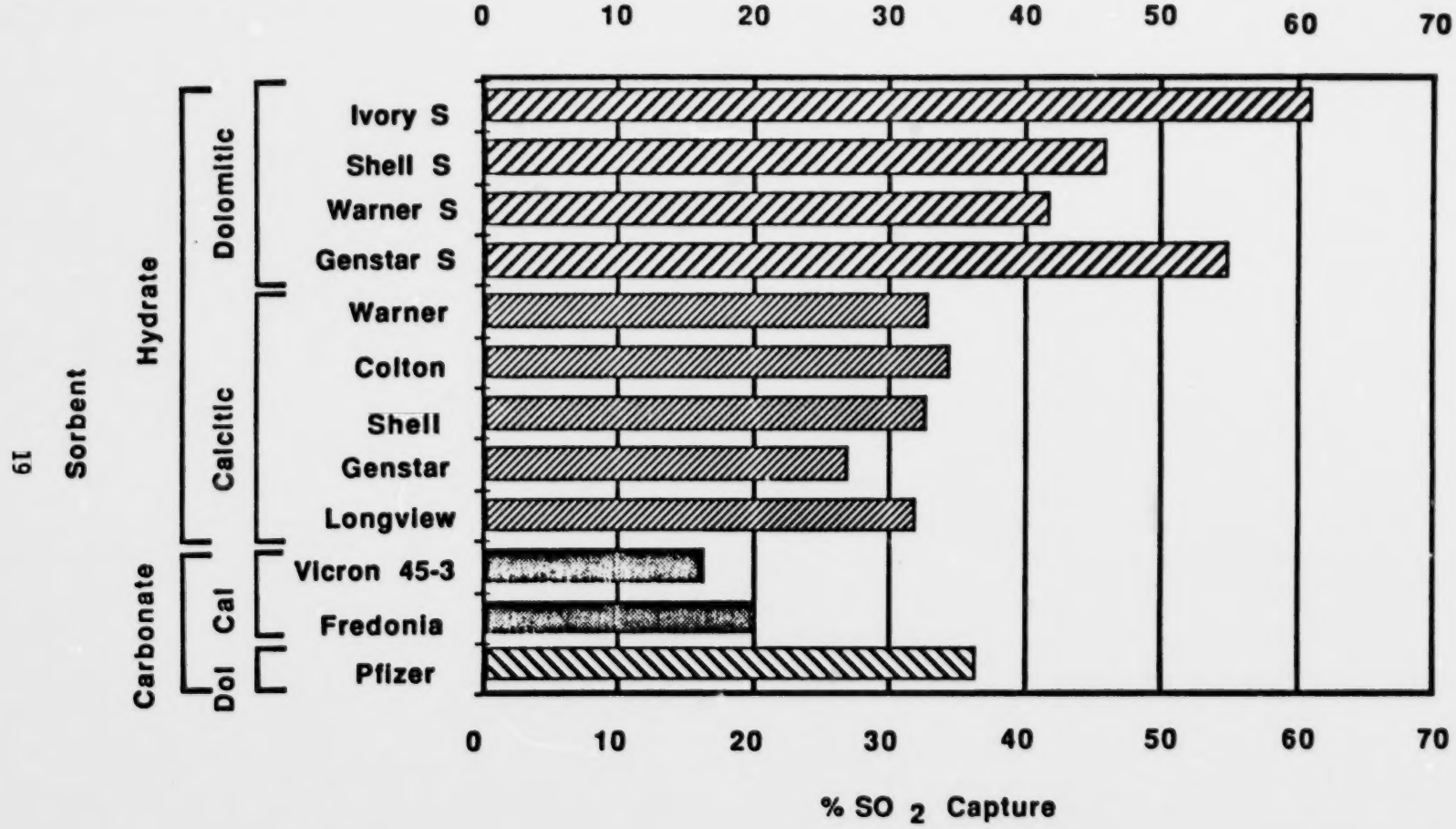

Figure 7. Comparison of Sorbent Sulfur Capture Data.

increasing surface area.

Figure 7 shows SO_2 capture data taken in a small scale furnace at 1090° C with a calcium to sulfur molar ratio of 2 and a residence time of 0.5 sec. The same trends are seen as in the surface area comparison. The hydrates perform better than the carbonates, and the dolomitic sorbents perform better than the calcitic sorbents. Again, the differences are greater between classes than within a class.

Figure 8 shows the percent SO_2 capture data of Figure 7 plotted against the surface area data of Figure 6. This simple relation with a correlation coefficient of 0.90 indicates that the surface area developed under inert calcination conditions provides a rough estimate of sorbent performance in an actual combustion environment.

In the sulfation experiments the residence time is much shorter and the temperature much higher than in the inert calcination experiment, yet the results correlate, suggesting that the controlling processes are identical. For the 700° C inert calcination, the surface area ranking is pressure hydrated dolomitic>>hydrated calcitic>>limestone. This ranking is the same for SO_2 sorption at 1090° C. Previous sulfation studies, Hartman and Coughlin (1976), and Silcox et al. (1985), have assumed that the calcination processes and the sulfation processes are completely sequential (calcination is complete before sulfation begins). The correlation of the data shown in Figure 8 suggests that sulfation may be coupled with calcination because the capture data do not correlate with the fully-calcined inert calcination results at long time (> 60 minutes) which show no difference in hydrate versus carbonate surface areas.

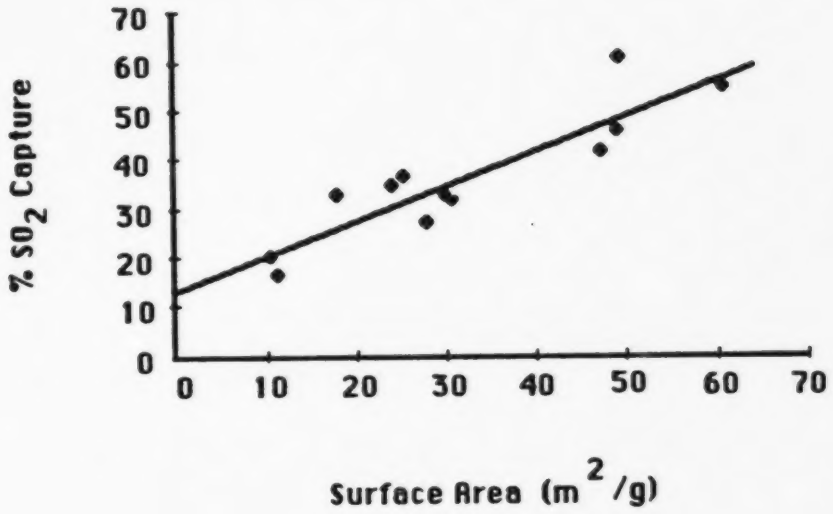

Figure 8. Correlation of Sulfation and Calcination Data.

CONCLUSIONS

The results of this study demonstrated major differences between some classes of sorbents. In general, the hydrated limes calcined faster and produced higher surface areas than the corresponding carbonates. The dolomitic sorbents also produced higher surface areas than the comparable calcitic sorbents. Pressure hydrated dolomitic limes performed the best, and limestones performed the worst. Variations within sorbent classes were generally smaller than differences between classes for the 14 sorbents studied in this work.

The surface area data indicate the existence of three simultaneous, competitive processes: calcination with an associated growth in surface area, catalyzed sintering which causes a rapid decrease in surface area, and deadburn sintering which results in a slow surface area loss. Deadburn sintering appears to only be significant above 700° C. Each of the competitive processes dominates in a particular regime during the overall calcination process.

In general, the surface areas obtained in this isothermal, inert calcination study correlate with SO_2 capture data taken in a small scale furnace at 1090° C, suggesting that, although the characteristic time constants are much shorter in an actual furnace environment, the controlling processes are similar.

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